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(54) **Thermoplastic compositions**

(57) A composition comprising (a) a carboxylated butadiene-acrylonitrile elastomer (b) an ethylene/(meth) acrylic acid copolymer at least partially neutralized, advantageously with a metal ion dynamically crosslinked by (c) an epoxy crosslinking agent.

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"Thermoplastic Compositions"

This invention relates to a thermoplastic elastomer, to a process for its manufacture, to a composition comprising the elastomer, and to an article made from the elastomer or a composition comprising it.

The thermoplastic elastomer of the invention is a polymer comprising units derivable from a butadiene-acrylonitrile polymer, some of which units are carboxylated, and units derivable from an ethylene/acrylic acid-based ionomeric polymer, the thermoplastic elastomer being crosslinked by an epoxy crosslinking agent. The elastomer of the invention may comprise units derivable from other moieties than those specified, although such moieties will advantageously be present in a minor proportion only, and the composition of the invention may comprise a polymer other than the polymer of the invention.

The composition may also comprise materials such, for example, as fillers, pigments, plasticizers, processing aids, stabilizers and antioxidants. Such materials may be incorporated to provide, modify, or enhance a given characteristic, for example, color, flexibility, or hardness.

The epoxy crosslinking agent may be any compound having more than one epoxy moiety; in the case of a crosslinking agent the molecule of which is clearly definable, the compound has at least two epoxy moieties per molecule; the crosslinking agent is sometimes referred to below as a "polyfunctional epoxy".

Although ionomers based on ethylene/acrylic acid copolymers are preferred, the terms "acrylic" and "acrylate" as used in this specification include both acrylic acid and methacrylic acid, and correspondingly, acrylates and methacrylates.

The elastomer of the present invention is advantageously produced by dynamic crosslinking of the carboxylated butadiene-acrylonitrile elastomer (herein sometimes referred to as XNBR) and the ionomer. Dynamic crosslinking, as the term is used herein, refers primarily to a procedure in which a composition comprising the elastomer, the ionomer, and the epoxy crosslinker is subjected to shear and, advantageously, heat.

More especially, the invention provides a thermoplastic elastomer produced from the dynamic crosslinking of a carboxylated butadiene-acrylonitrile elastomer and an ionomeric ethylene/acrylic acid copolymer using an epoxy crosslinking agent having a minimum of two epoxy moieties per molecule (a polyfunctional epoxy). The compositions of the instant invention may provide a thermoplastic elastomer having the advantages both of being an easily processed thermoplastic elastomer and of having the superior physical properties of conventional vulcanized rubbers.

The compositions of the instant invention may be used to provide articles such, for example, as hoses,

belts, wire and cable insulation, footwear, mechanical goods and a wide variety of other rubber products. These thermoplastic elastomers may be extruded, injection-molded or calendered.

The present invention provides a thermoplastic elastomer characterized by the presence of both ionic bonds and covalent bonds. The ionic bonds are formed by the partial neutralization of the carboxyl groups on both polymers. The covalent bonds are formed by the reaction of the polyfunctional epoxy crosslinker with the carboxyl groups present in both the elastomer and the ionomeric copolymer. The presence of both ionic and covalent bonds provides a thermoplastic elastomer having the easy processing characteristics which are typical of ionic polymers and also provides superior physical properties.

The instant invention provides a thermoplastic elastomer having both superior physical characteristics and superior processing capabilities allowing it to be easily processed. Such a thermoplastic elastomer more especially comprises a dynamically crosslinked blend of: (a) a carboxylated butadiene-acrylonitrile elastomer (XNBR) and (b) an ethylene/acrylic acid copolymer which has been at least partially metal ion neutralized (an ionomer of ethylene and acrylic acid) wherein (a) and (b) have been dynamically crosslinked with a polyfunctional epoxy crosslinking agent.

The polyfunctional epoxy crosslinking agent may be any compound having more than one epoxy moiety. The ethylene/acrylic acid copolymer must have been at least partially neutralized, advantageously with a metal ion, to provide ionic crosslinking in addition to the dynamic crosslinking. Advantageously, the minimum amount of metal ion is that amount of metal needed to provide 0.5 parts of metal per 100 parts of total polymer. Throughout this specification, "parts" are parts by weight.

The dynamic crosslinking reaction that produces the instant composition may be induced by applying shear and heat to a mixture of the elastomer, the ionomer, and the epoxy crosslinker.

The polyfunctional epoxy crosslinker should advantageously be present in the amount needed to provide a minimum of 0.010 parts of oxirane oxygen per hundred parts of total polymer (PhP).

The thermoplastic elastomer of the invention may preferably be prepared by dynamically crosslinking a homogeneous mixture of the XNBR and the ethylene/acrylic acid copolymer (or ionomer) with the crosslinker normally at elevated temperatures (over 135°C). Shear should be provided during crosslinking. If a metal salt is to be separately added, it may be mixed in either before or after dynamic crosslinking. The polyfunctional epoxy should

either a) be well blended before raising temperatures to induce dynamic crosslinking, or b) be added carefully to the homogeneous blend during mixing; in order to obtain a uniformly crosslinked product.

"Dynamic" crosslinking means that, while the crosslinking reaction occurs (with the polyfunctional epoxy), shear stress is applied to the mixture. Conventional vulcanization is avoided, and a product is produced which may be melted again for combination with other ingredients or for forming into a finished product. The product may also be extruded, compression molded, or injection molded into a desired shape.

The concentrations of the XNBR, the epoxy crosslinker, the ethylene/acrylic acid copolymer and the neutralizing metal ion may all be widely varied. In this manner, any particularly desired characteristic can be obtained.

Advantageously, the concentration of the carboxylated butadiene-acrylonitrile elastomer is within the range of from about 90 to about 10 PhP. The concentration of the ethylene/acrylic acid ionomer advantageously correspondingly ranges from about 10 to about 90 parts PhP, although the presence of other units in the polymer is within the scope of the invention. The polyfunctional epoxy crosslinking agent should advantageously be present in an amount sufficient to provide a minimum of about 0.01 parts of oxirane oxygen PhP.

The preferred range for the carboxylated butadiene-acrylonitrile elastomer is from about 80 to about 15 PhP, while the most preferred concentration range is from about 75 to about 20 PhP. A preferred concentration range for the ionomer is from about 20 to about 85 PhP, while the most preferred concentration range is from about 25 to about 85 PhP.

Advantageously, the oxirane oxygen level of the polyfunctional epoxy crosslinker is in the range of from about 0.01 to about 7.0 PhP. A more preferred range, however, is from about 0.020 to about 3 PhP and the most preferred range is from about 0.030 to about 2.5 PhP.

As indicated above, there is advantageously a minimum of 0.5 part of the neutralizing metal ion PhP present in the elastomer-ionomer mixture in order to provide ionic bonding. An advantageous concentration range is from about 0.5 to about 30 parts of metal per hundred parts of resin. A more preferred range is from about 3 to about 15 parts per hundred parts of resin. An even more preferred range is from about 5 to about 10 parts of metal per hundred parts of resin. Advantageously, there should be a minimum of 1 part of free acid (unneutralized acrylic acid after the addition of the metal ion but before crosslinking) PhP and preferably 2 or more parts free acid PhP. A preferred range of unneutralized free acid is from about 1 to about 20 parts PhP.

A polyfunctional epoxy crosslinking agent is any compound having more than one epoxy functionality per molecule. Numerous such compounds are commercially available.

Any polyfunctional epoxy compound may be used as the crosslinking agent for this composition. Acceptable epoxy crosslinking agents are epoxidized soy oil, epoxidized linseed oil, epoxidized tall oil or epoxidized natural rubber. An acceptable epoxidized crosslinking agent may also be selected from the group consisting of: an epoxidized alkyl glycidyl ether, an epoxidized polyglycidyl ether of phenol, an epoxidized glycidyl ether of an aromatic compound, an epoxy cycloalkyl carboxylate, an epoxidized glycidyl ether of an aliphatic polyol, an epoxidized thioglycidyl resin, a glycidyl ester, an epoxidized polybutadiene, an epoxidized unsaturated polyester, a mixture of any two or more of such compounds or a mixture of any one or more such compounds with one or more other unspecified polyfunctional epoxy compounds.

A preferred polyfunctional epoxy crosslinking agent is one selected from polyphenol formaldehyde poly(2,3-epoxypropyl) ether; 3,4-epoxycyclohexylmethyl - (3,4-epoxy)cyclohexane carboxylate; poly(2,3-epoxy propyl) ether carboxylate, tetraglycidoxy tetraphenyl-ethane, 2,2-bis[4-(2,3-epoxypropoxy)-3,5-dibromophenyl] propane and epoxidized diallycidyl ether of Bis Phenol A.

Of these, it is to be noted that 3,4-epoxy-cyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate is an excellent crosslinker, having good crosslinking activity and a moderately fast reaction rate.

The carboxylated butadiene-acrylonitrile polymer should advantageously contain a minimum of 1% by weight of the carboxylated monomer. An advantageous range for the concentration of the carboxylated units is from about 1 to about 20% by weight. A preferred range is from about 2.5 to about 15% by weight of carboxylated monomer and the most preferred concentration range for the carboxylated monomer is from about 3 to about 10% by weight. The acrylonitrile monomer may advantageously be present in a range of from about 15 to about 50% by weight; preferably, it is present in a range of from about 18 to about 45% by weight, and more preferably in a concentration range of from about 20 to about 40% by weight. Carboxylated butadiene-acrylonitrile polymers are commercially available from, for example, such sources as Polysar, Goodyear, and Goodrich.

Ethylene/acrylate ionomers and ethylene/acrylic acid copolymers are both commercially available. If desired an ethylene/acrylate ionomer may be directly utilized or an ethylene/acrylate copolymer may be used and an appropriate amount of metal ion provided by adding a metal salt. Suitably, the metal salt may be

added by melt blending, either before or after the dynamic crosslinking. Even when using a commercially available ionomer, it is permissible to increase the concentration of the metal ion by adding a metal salt before or after dynamic crosslinking. Preferably, a metal oxide is used.

The acrylate moiety of the ionomer should advantageously be present in a minimum amount of about 1.0 parts PhP. An advantageous range for the acrylate moiety (including both neutralized and unneutralized acrylate) is from about 1.0 to about 50 parts PhP. A preferred range is from about 5 to about 30 parts PhP and an even more preferred range is from about 10 to about 25 parts PhP.

The neutralizing metal ion, as previously indicated, may be provided by the addition of a metal salt. Any metal salt may be used. Preferably, a metal oxide is used. Although generally the metal ion utilized may be any metal (and any metal salt) preferred metals are selected from groups I and II of the Periodic Table. More preferred metals are zinc, sodium, calcium and magnesium, the oxides or hydroxides of these metals being most preferred.

From the discussion thus far, it will be appreciated that the process for the preparation of the instant invention has several embodiments. It is ~~permissible to use ethylene/acrylic acid copolymer or~~

ionomer in the blend with the XNBR, with the addition of the metal ion to provide an increase in ionic crosslinking. The metal ion (in the form of a metal salt) may furthermore be added either before or after dynamically crosslinking with the polyfunctional epoxy crosslinker.

It is also possible to vary the temperature at which the crosslinker is added. Furthermore, if the crosslinker is added at temperatures under 130°C (generally 100-130°C), the crosslinker may be mixed with either the XNBR or the ethylene/acrylic acid copolymer (or ionomer) before or after the addition of the other ingredient(s).

In a preferred embodiment the process comprises homogeneous blending of 1) the XNBR, 2) the polyfunctional epoxy crosslinker and 3) the ionomer or the ethylene/acrylic acid copolymer at a temperature less than 135°C (preferably from about 110 to about 130°C). The ingredients may be added in any convenient order. After the homogeneous blend is obtained, the temperature is increased (over 135°C) to obtain dynamic crosslinking. Elevated temperatures are desirably maintained until dynamic crosslinking has been completed, the temperature advantageously being kept lower than 200°C. A preferred temperature range is from about 140°C to about 185°C.

When desired, a metal salt may be added at any

convenient time either before or after dynamic crosslinking. When the metal ion is added afterward, the composition should be melt blended until a homogeneous composition is obtained.

While the composition may be prepared by the addition of the crosslinker to the blend at temperatures in excess of 135°C and less than 200°C in a manner effective to produce uniform crosslinking, it is preferred not to elevate the temperatures until after a uniform dispersion of the crosslinker is obtained. This will avoid non-uniform or inferior products which would result from crosslinking a poorly mixed combination.

Suitable mixing apparatus includes, for example, mills, internal mixers, extruders, and other apparatus in common use in the rubber and plastics industry.

The level of covalent crosslinking is varied by increasing or decreasing the oxirane oxygen concentration and/or the level of the available carboxy functionalities in the resin. Because this dynamic (covalent) crosslinking is provided, the instant composition is capable of providing a higher temperature use range than an ionically crosslinked blend of the two polymers. The instant composition also provides superior flexibility, lower tensile set, and higher tear strength. The covalent crosslinking (possibly within the individual polymers as well as

between the two polymers), in combination with the ionomer characteristics of the blend, raises the use temperature and improves overall physical properties.

The characteristics of the instant thermoplastic elastomer may be controlled and varied by increasing or decreasing the concentration of the elastomer, the ionomer, the ionic bonding, and/or by increasing or decreasing the level of dynamic crosslinking. In addition to this, it is also within the scope of the instant invention to use plasticizers, pigments, fillers, stabilizers, and antioxidants in the thermoplastic elastomer. Such additives may be added at any time in the mixing sequence. Thus, they may be added to the mixture and homogeneously mixed in at any point before or after dynamic crosslinking, or the finished product may even be reheated and the additives blended in.

The instant invention may be readily understood from the examples that follow.

The following examples include data collected from ASTM tests performed on the finished dynamically crosslinked product. Test samples were prepared, and individual specimens for the tests were cut from the sample. The test samples were prepared by compression molding in a 6 x 6 in x 0.075 in (about 150 mm x 150 mm x 1.9 mm) mold at 175°C (unless otherwise indicated)

using a molding cycle of a two minute warm up without pressure, two minutes under 800 psi (5.5 MPa) and a cool down to 65°C under pressure before removing from mold. The tests performed and their ASTM numbers are:

Hardness, Shore "A" ASTM D2240

Tensile Strength, Modulus ASTM D412
and Elongation Method A

Immersion, Vol. change in oil. ASTM D471

Compression set ASTM D395 Method B

Melt Index ASTM D1238

The tear resistance, Brown initial strength, measurement was taken in accordance with the following procedure: condition test specimens for 24 hours at 23±1°C and 50±2% relative humidity. Three 4 in x 2 in (about 1000 mm x 50 mm) U-shaped test specimens were cut from the test sample. The following procedure was used: (a) Mount test specimens in Instron Tensile Tester by clamping the two legs of the specimen in the jaws of the Instron Tester, (b) Set jaw separation at 1 in (about 25 mm) and Instron gauge at 0, then pull jaws apart at a constant speed of 12 in/min (about 305 mm/min), (c) Record initial tear strength. Test value is the average obtained from three specimens of the same sample.

Example 1

Sample blends 1-5 were prepared by mixing the carboxylated butadiene-acrylonitrile elastomer (Krynac

211) at temperatures within 120-130°C with the sodium-ethylene/acrylic acid ionomer (Surlyn* 8920). The epoxy crosslinker was added, homogeneously mixed, and the temperature was increased to 155°C. The crosslinking agent used was the epoxy hydrocarbyl crosslinking agent Paraplex* G-62, an epoxidized soy oil (approximately 6.8% by wt. oxirane oxygen).

When no epoxy crosslinker was added, the temperature was increased to 155°C after the initial mixing of the two polymers, and the blend was mixed for five more minutes, allowing interaction between the free carboxyl units of the carboxylated nitrile polymer and the metal ion of the ionomer. Such a procedure produces a mixed ionomer of the two polymers.

Similar blends, both with and without the epoxy crosslinker, of the copolymers are compared in the following table. This series shows that dynamic crosslinking is induced with the instant epoxidized crosslinkers to produce thermoplastic elastomers over a wide range of polymer ratios.

* Trade Marks

Table 1

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|---------------------------|
| 1 Krynac 211 | 90 | | | | | |
| Surlyn-Na | 10 | 135 | 670 | 750 | 55 | -- |
| WITH 2 PARTS Epoxy | | 210 | 860 | 375 | 59 | 37 |
| 2 Krynac 211 | 75 | | | | | |
| Surlyn-Na | 25 | 375 | 770 | 580 | 75 | 38 |
| WITH 2 PARTS Epoxy | | 450 | 1250 | 340 | 80 | 54 |
| 3 Krynac 211 | 50 | | | | | |
| Surlyn-Na | 50 | 970 | 2060 | 395 | 93 | 67 |
| WITH 2 PARTS Epoxy | | 1120 | 2310 | 265 | 94 | 91 |
| 4 Krynac 211 | 25 | | | | | |
| Surlyn-Na | 75 | 1800 | 3410 | 315 | 96 | 82 |
| WITH 2 PARTS Epoxy | | 2100 | 3450 | 205 | 97 | -- |
| 5 Krynac 211 | 10 | | | | | |
| Surlyn-Na | 90 | 2270 | 3710 | 265 | 98 | 83 |
| WITH 2 PARTS Epoxy | | 2500 | 3590 | 155 | 97 | -- |

In this and subsequent tables pounds per square inch (PSI) may be converted to MPa by multiplying by 0.00689. Conversion of Brown Tear (lb) to Brown Tear (Kg) may be effected by multiplication by 0.454.

In the above example, it should be noted that the materials which were prepared with no epoxy (having only ionic crosslinking and no covalent crosslinking),

could only be removed from the mill in a whole sheet by first cooling the mill to temperatures between 100-110°C. The blends which were covalently crosslinked with epoxy crosslinker, however, were easily removed from the mill as a single sheet without cooling, thus demonstrating good processing characteristics at temperatures of 150-155°C.

Example 2

Sample blends 6-10 were prepared according to the following general procedure. The carboxylated butadiene-acrylonitrile elastomer used herein, containing approximately 9% carboxylated monomer, and approximately 25-29% acrylonitrile monomer (Krynac 211 marketed by Polysar, Inc.) was blended in the amount indicated below for each sample along with the specified amount of Surlyn 8920 (copolymer of ethylene/acrylic acid with sodium). The blends were made by blending the two polymers on a laboratory mill at 150-155°C. After the initial blending, milling was continued at this temperature for five minutes to induce any interaction between the free carboxylated units of the carboxylated nitrile polymer and the metal ion of the ionomer. Such a blending procedure produces a "mixed" ionomer of the two polymers. Milling characteristics of this "mixed" ionomer were such that the temperature of the mixing mill had to be reduced to 100-110°C before the composition could be removed

from the mill as a single sheet. For samples 7-10, the epoxy hydrocarbyl crosslinking agent, Paraplex* G-92 epoxidized soy oil, was added to the blend after the initial blending of the two polymers, and milling was continued at 150-155°C for five more minutes to produce the dynamically crosslinked product. During the procedure, crosslinking activity was apparent after two to three minutes of milling. As the dynamic crosslinking takes place the mix shows greater cohesion, less mill tack, higher viscosity, and increased elasticity. At the more desirable levels of crosslinking (less than 5 parts) a smoother milled sheet having more uniform flow and better processing is produced. The crosslinked blends were easily removed from the 150-155°C mill as a single sheet without the cooling which is required when no dynamic crosslinking is present.

Table II

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|------------------------------------|-----------------|-----------------|-------------|----------|------------------|------------------------|
| 6 Krynac 60 Surllyn-Na Epoxy | 60 40 0 | 670 | 1880 | 445 | 86 | 59 |
| 7 Krynac Surllyn Epoxy | 60 40 1 | 810 | 2150 | 400 | 88 | 87 |
| 8 Krynac Surllyn Epoxy | 60 40 2 | 930 | 2440 | 335 | 87 | 89 |

* Trade Mark

Table II (continued)

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|------------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|---------------------------|
| 9 Krynac Surlyn Epoxy | 60 40 3 | 935 | 2350 | 275 | 89 | 92 |
| 10 Krynac Surlyn Epoxy | 60 40 5 | 920 | 2200 | 215 | 90 | 67 |

Example 3

An ethylene/acrylic acid copolymer (Et/Ac copolymer) was used (Primacor* 435 manufactured by Dow Chemical). The acrylic acid monomer content is approximately three percent. This example demonstrates the need for both ionic and covalent bonds to produce the desired thermoplastic elastomer with good processing characteristics and physical properties. The elastomer used was that described in Example 2. The elastomer, (XNBR), the ethylene/acrylic acid copolymer, and the zinc oxide were added and mixed in the amounts shown in the table below at a temperature of 120-130°C. The epoxy crosslinker (the epoxidized soy oil - Paraplex G-62 having about 6.8% oxirane content) was added in the amounts indicated below after which time the temperature was increased to 155°C. The mixture was blended for five minutes while crosslinking occurred to complete the thermoplastic elastomer.

* Trade Mark

Table III

| Sample | 11 | 12 | 13 | 14 |
|---------------------------------|-------|-------|-------|--------|
| XNBR | 60 | 60 | 60 | 60 |
| Et/Ac copolymer | 40 | 40 | 40 | 40 |
| Epoxy | -- | 2 | 3 | 2 |
| ZnO | -- | -- | -- | 5 |
| 50% modulus, psi | 360 | 420 | 410 | 730 |
| Tensile, psi | 360 | 490 | 580 | 1,650 |
| Elongation, % | 60 | 250 | 330 | 365 |
| Hardness, Shore A | 81 | 81 | 81 | 91 |
| Brown Tear, lb | 17 | 20 | 25 | 66 |
| Milled Sheet Characteristics | Rough | Pough | Rough | Smooth |

The above blends which were "rough", were undesirable (lumpy, had holes, and did not have a smooth texture).

Example 4

Sample blends 15-18 were prepared according to the procedure explained in Example 2. The same carboxylated butadiene-acrylonitrile elastomer (Krynac 211) was used; the other copolymer was a copolymeric ethylene/zinc acrylate ionomer (Surlyn 9020) in the amounts shown in the table below. The same crosslinking agent (Paraplex G-62) was used as in Example 1.

Table IV

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|---------------------------|
| 15 XNBR Ionomer Epoxy | 60 40 0 | 350 | 1030 | 685 | 79 | 41 |
| 16 XNBR Ionomer Epoxy | 60 40 1 | 410 | 1640 | 555 | 79 | 48 |
| 17 XNBR Ionomer Epoxy | 60 40 2 | 410 | 1470 | 440 | 78 | 50 |
| 18 XNBR Ionomer Epoxy | 60 40 3 | 435 | 1560 | 340 | 79 | 52 |

For the above described mixture excellent processing characteristics and good physical properties are shown at epoxy levels between 1 and 2.0 PhP (preferred 1.5-2.0 PhP).

Comparative Example 5

This is a comparative example wherein the crosslinker used in Examples 1-4 is blended in varying amounts with the same (XNBR) used in Examples 1-4. These two ingredients were blended on a laboratory mill at 150-155°C and compression molded at 175°C with cool down under pressure.

During the milling operation, it was obvious that the XNBR was crosslinked. This composition is

undesirable; good physical properties do not develop. When the crosslinking concentration is high enough to increase tensile strength, the milled sheet itself becomes rough, full of holes, and crumbly. The following table shows samples 19-21 which were prepared with similar amounts of the same crosslinker used in the previous Examples. The blends of the table below thus only had dynamic (covalent) crosslinking.

Table V

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A |
|--------------------------|-----------------|---|-------------|----------|------------------|
| 19 XNBR Epoxy | 100 1 | 92 | 400 | 495 | 49 |
| 20 XNBR PAR-62 | 100 2 | 92 | 500 | 440 | 49 |
| 21 XNBR PAR-62 | 100 3 | Milled sheet was rough and lumpy, full of holes and did not flow in the mold well enough to form a good sample. | | | |

Comparative Example 6

The following sample blends 22-27 were prepared with either the sodium ionomer, Surllyn 8920, or the zinc ionomer, Surllyn 9020. The epoxy crosslinker used was Paraplex G-62 also used in previous examples. Test samples 22-27 were prepared by milling at 150-155°C. Test specimens were compression molded at 175°C with cool down under pressure. Table VI shows the results of testing done on these samples.

Table VI

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Melt Index* |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|----------------|
| 22 Surlyn 8920 | 100 | 2475 | 4470 | 275 | 97 | 48.7 |
| 23 Surlyn 8920 Epoxy | 100 1 | 2560 | 4340 | 230 | 95 | 1.1 |
| 24 Surlyn 8920 Epoxy | 100 2 | 2660 | 3290 | 110 | 95 | — |
| 25 Surlyn 9020 | 100 | 1240 | 2730 | 340 | 94 | — |
| 26 Surlyn 9020 Epoxy | 100 0.5 | 1530 | 2670 | 215 | 95 | — |
| 27 Surlyn 9020 Epoxy | 100 1.0 | 1540 | 2750 | 200 | 94 | — |

* Melt Index = g/10 min at 375°C (about 190°C) and 433 PSI (2.98 MPa) (ASTM D1238).

The samples above show both the sodium ionomer, Surlyn 8920 and the zinc ionomer, Surlyn 9020 alone, using the same epoxy crosslinker as was used in Example 2. Both polymers show rapid increases in viscosity on the mixing mill at very low levels of addition of the crosslinker; as low as one part for the sodium and as low as 0.5 for the zinc; with the zinc showing a more rapid viscosity increase than the sodium. At the higher levels of crosslinker the viscosity increased to

a point where the polymer could no longer be effectively processed, as indicated by the low melt index. Such compositions could not be satisfactorily extruded or injection molded.

Unlike the individual polymers, blends of a carboxylated butadiene-acrylonitrile elastomer and a metal-ion neutralized ethylene/acrylic acid copolymer can be dynamically crosslinked with the polyfunctional epoxy compounds to produce a thermoplastic elastomer having good physical properties and excellent processing characteristics.

Example 7

In this Example, the XNBR elastomer used was Krynac 231 marketed by Polysar, Ltd. which had approximately 7% carboxylated monomer and a level of acrylonitrile monomer in the range of 30-33%. This XNBR is shown in Sample 28. Another XNBR which was evaluated was NX 775 by Goodyear which also contained approximately 7% carboxylated monomer (Sample 29), but had an acrylonitrile monomer content of about 28%. The ionomer was Surlyn 8920.

These blends were prepared in accordance with the procedures given for Example 2.

Table VII

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|---------------------------|
| 28 Krynac-231 | 60 | | | | | |
| Surlyn 8920 | 40 | 530 | 1190 | 485 | 86 | 52 |
| With Epoxy | 2 | 920 | 1890 | 325 | 89 | 75 |
| 29 NX 775 | 60 | | | | | |
| Surlyn 8920 | 40 | 570 | 685 | 299 | 87 | 36 |
| With Epoxy | 2 | 740 | 2100 | 340 | 89 | 76 |

Example 8

This Example shows that fillers, antioxidants and processing aids may be added to the dynamically crosslinked blend for purposes such as improving processing, increasing stiffness and hardness or lowering costs. The XNBR used was Krynac 211. The ionomer used was Surlyn 8920 ionomer previously described, the epoxy crosslinking agent used was Paraplex G-62. All of these were used in the amounts indicated in the table below. The sample below was prepared in accordance with the following procedure. The XNBR copolymer and the Surlyn 8920 ionomer were melt blended on a laboratory mill at 150-155°C. After the initial blending, the FEF Black, Carbowax* 4000, and Agerite* Superlite (di-8-naphthyl-p-phenylene-diamine) were added, followed by the Paraplex G-62

* Trade Marks

(epoxy). After the addition of all materials, milling was continued for five minutes at the 150-155°C mill temperature until the dynamic crosslinking had been completed. The table below shows the amounts of each ingredient and the results of tests conducted on this sample.

Table VIII

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|---------------------------|
| 30 XNBR | 60 | | | | | |
| Ionomer | 40 | | | | | |
| Epoxy | 2 | | | | | |
| Agerite | | | | | | |
| Superlite | 1 | | | | | |
| Carbowax | 2 | | | | | |
| FEF Black | 15 | 1390 | 2220 | 175 | 94 | 85 |

Example 9

This example demonstrates a preferred method for the preparation of the instant thermoplastic elastomer. The method applied in this example results in dynamically crosslinked thermoplastic elastomers which have more uniform physical and processing characteristics.

Accordingly, samples 31 to 38 of Table IX below were prepared by blending the epoxidized natural rubber crosslinking agent (epoxy in the table below) on a cold laboratory mixing mill with the XNBR. The blend was then melt blended with the ionomer at 120°C. After

the mixture was blended uniformly, the temperature was raised to 147-156°C and milling continued for five minutes, to induce more rapid corsslinking. The thermoplastic elastomer produced was easily processed on conventional thermoplastic processing equipment. The table below give the test results of the samples prepared according to the above procedure. The addition of zinc oxide to increase the overall ion content of the composition shows only a slight increase in modulus and reduction in elongation.

Table IX

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A |
|--|-----------------------|-----------------------|----------------|-------------|---------------------|
| 31 Krynac 221 Surlyn 8920 Epoxy | 55 35 10 | 704 | 2325 | 352 | 88 |
| 32 Krynac 211 Surlyn 8920 Epoxy ZnO | 55 35 10 5 | 812 | 2259 | 320 | 87 |
| 33 Krynac 211 Surlyn 8920 Epoxy | 50 35 15 | 870 | 2003 | 198 | 88 |
| 34 Krynac 211 Surlyn 8920 Epoxy ZnO | 50 35 15 5 | 906 | 2484 | 273 | 90 |
| 35 Krynac 211 Surlyn 8920 Epoxy | 45 35 20 | 812 | 2492 | 307 | 90 |

Table IX (continued)

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|
| 36 Krynac 211 | 45 | | | | |
| Surlyn 8920 | 35 | | | | |
| Epoxy | 20 | | | | |
| ZnO | 5 | 874 | 2413 | 290 | 90 |
| 37 Krynac 211 | 60 | | | | |
| Surlyn 9020 | 40 | | | | |
| Epoxy | 3 | | | | |
| ZnO | 5 | 550 | 1384 | 483 | 82 |
| 38 Krynac 211 | 60 | | | | |
| Surlyn 9020 | 40 | | | | |
| Epoxy | 5 | | | | |
| ZnO | 5 | 555 | 1460 | 446 | 82 |

Krynac 211 was the carboxylated butadiene-acrylonitrile elastomer (XNBR of Example 2) (9% carboxylated monomer and approximately 25-29 percent acrylonitrile monomer). The epoxy, an epoxidized natural rubber (ENR-50), contained approximately 50 mole percent epoxidation of the double bonds. The epoxidation has been shown to be random.

Example 10

The compositions were mixed in the same manner as sample 7-10 of Example 2 except that the three polymers were melt blended together before the addition of the Paraplex G-62 epoxy crosslinker. After the addition of the Paraplex G-62, milling was continued at the 150-155°C mixing temperature for five minutes to complete dynamic crosslinking.

Elvax* 360, an ethylene/vinyl acetate copolymer (containing approximately 25 percent vinyl acetate) was added as a solid plasticizer or modifier and which effectively reduced modulus and hardness without severely limiting tensile strength, elongation, and tear strength. Elvax 360 (a non-reactive thermoplastic resin) does not dynamically crosslink or enter into the ionic structure of the thermoplastic elastomer.

Table X

| <u>Sample No.</u> | <u>39</u> | <u>40</u> | <u>41</u> |
|-------------------------|-----------|-----------|-----------|
| Krynac 211 | 60 | 60 | 50 |
| Surlyn 8920 | 30 | 25 | 35 |
| Elvax 360 | 10 | 15 | 15 |
| Paraplex G-62 | 3 | 3 | 2.5 |
| 50% Modulus, PSI | 610 | 515 | 745 |
| Tensile, PSI | 1,780 | 1,500 | 2,080 |
| Elongation, % | 280 | 280 | 330 |
| Hardness, Shore A | 83 | 80 | 87 |
| Brown Tear, Initial lb. | 47 | 52 | 60 |

Example 11

In this example, the elastomer, Krynac 211, and the ionomer, Surlyn 8920, were homogeneously blended in the amounts indicated in the table below at a temperature of 120-130°C. The epoxy crosslinker used was added

* Trade Mark

during mixing and the temperature was then increased to 155°C, and the mixture was blended for 5 more minutes while crosslinking occurred to complete the thermoplastic elastomer.

This example shows that this invention is not limited to the crosslinking activity of any one particular polyfunctional epoxy, and demonstrates that any miscible polyfunctional epoxy compound could be used as the dynamic crosslinker. Concentrations required to produce the desired processing characteristics and physical properties of the resulting thermoplastic elastomer will depend on the molecular structure and the overall oxirane content. Preferably, the oxirane content of the polyfunctional epoxy crosslinker is between 5 and 15 percent by wt. The following epoxy compounds were evaluated.

| <u>Code</u> | <u>Trade Name</u> | <u>Chemical Name</u> | <u>Manufacturer</u> |
|-------------|--------------------|--|---------------------|
| A. | Drapex* 10.4 | Epoxidized Linseed Oil | (Argus) |
| B. | Drapex 4.4 | 4,4'-octyl epoxy tallate | (Argus) |
| C. | Epon* 828 | Diglycidyl ether of bisphenol A | (Shell) |
| D. | Araldite* EPN 1138 | Polyglycidyl ether of phenol-formaldehyde novolac | (Ciba-Geigy) |
| E. | Araldite CY 179 | 3,4-Epoxy cyclohexylmethyl - (3,4-epoxy) cyclohexane carboxylate | (Ciba-Geigy) |
| F. | Epon 1031 | Tetraglycidoxy tetraphenylethane | (Shell) |

* Trade Marks

G. EPI Rex 5163 Diglycidyl ether of (Celanese)
tetrabromo bisphenol A

H. Araldite RD1 n-butyl glycidyl ether (Ciba-Geigy)

Table XI

| Sample No. & Ingredients | Parts By Weight | 50% Modulus PSI | Tensile PSI | Elong. % | Hardness Shore A | Brown Tear Initial lb. |
|-----------------------------|-----------------------|-----------------------|----------------|-------------|---------------------|---------------------------|
| 42 Krynac 211 | 60 | | | | | |
| Surlyn 8920 | 40 | 670 | 1800 | 445 | 86 | 59 |
| 43 With Epoxy A | 2 | 900 | 2360 | 300 | 89 | 89 |
| 44 Epoxy B | 2 | 600 | 1630 | 300 | 87 | 63 |
| 45 Epoxy C | 2 | 915 | 2160 | 290 | 90 | 66 |
| 46 Epoxy C | 5 | 1220 | 2410 | 200 | 90 | 70 |
| 47 Epoxy D | 2 | 780 | 1700 | 235 | 89 | 57 |
| 48 Epoxy E | 1 | 750 | 2340 | 440 | 90 | 84 |
| 49 Epoxy E | 2 | 800 | 1960 | 285 | 90 | 70 |
| 50 Epoxy F | 2 | 740 | 1780 | 265 | 88 | 44 |
| 51 Epoxy F | 4 | 870 | 1970 | 195 | 90 | 49 |
| 52 Epoxy G | 2 | 700 | 1320 | 250 | 90 | 43 |
| 53 Epoxy G | 4 | 840 | 1420 | 185 | 90 | 50 |
| 54 Epoxy H | 2 | 575 | 1230 | 380 | 85 | 37 |

Crosslinking is indicated by increases in one or more of modulus, hardness and tear strength and a reduction in elongation. Preferred crosslinkers also increase tensile. Epoxy H, n-butyl glycidyl ether, a monofunctional epoxy molecule does not effect crosslinking. Instead, it has a plasticizing effect and reduces modulus, tensile, elongation, hardness and tear strength.

CLAIMS

1. A thermoplastic elastomeric composition comprising a dynamically crosslinked blend of (a) a carboxylated butadiene-acrylonitrile elastomer and (b) an ethylene/acrylic acid copolymer which has been at least partially neutralized; wherein (a) and (b) have been dynamically crosslinked with a polyfunctional epoxy crosslinking agent.
 2. A composition as claimed in claim 1, wherein the carboxylated butadiene-acrylonitrile elastomer is present in an amount in the range of from about 10 to about 90 parts by weight; and wherein the ethylene/acrylic acid copolymer is present in an amount in the range of from about 90 to about 10 parts by weight based on the total weight of component a) and b).
 3. A composition as claimed in claim 1 or claim 2, wherein the epoxy crosslinking agent is present in an amount sufficient to provide a minimum of 0.010 parts of oxirane oxygen PhP (per hundred parts polymer, by weight).
 4. A composition as claimed in any one of claims 1 to 3, wherein the carboxylated monomer content of elastomer (a) is in the range of from about 2.5-15% by weight of the elastomer.
 5. A composition as claimed in any one of claims 1 to 3, wherein the polyfunctional epoxy crosslinking agent is selected from epoxidized soy oil, epoxidized
-

linseed oil, epoxidized tall oil and epoxidized natural rubber.

6. A composition as claimed in any one of claims 1 to 5, wherein the epoxy crosslinking agent is selected from an epoxidized alkyl glycidyl ether, an epoxidized polyglycidyl ether of phenol, an epoxidized glycidyl ether of an aromatic compound, an epoxy cycloalkyl carboxylate, an epoxidized glycidyl ether of an aliphatic polyol, an epoxidized thioglycidyl resin, a glycidyl ester, an epoxidized polybutadiene, and an epoxidized unsaturated polyester.

7. A composition as claimed in any one of claims 1 to 6, wherein the ethylene/acrylic acid copolymer has been neutralized by metal ions.

8. A composition as claimed in claim 7, wherein the metal ion is selected from the metals of Group I and II of the Periodic Table.

9. A composition as claimed in claim 7 or claim 8, wherein the metal ions are present at at least 0.5 parts PhP.

10. A composition as claimed in any one of claims 1 to 9, which also contains at least one component selected from a filler, an antioxidant, a pigment and a plasticizer.

11. A composition as claimed in any one of claims 1 to 10, which was prepared by mixing at less than 130°C a homogeneous blend of the carboxylated

butadiene-acrylonitrile elastomer, the epoxy crosslinking agent, and a copolymer of ethylene/acrylic acid and increasing the temperature to in excess of 135°C and mixing for a sufficient length of time to allow dynamic crosslinking, and then blending in a metal salt to form a homogeneous product.

12. A composition as claimed in any one of claims 1 to 10, which was prepared by mixing a homogeneous blend of the (a) elastomer, the polyfunctional epoxy crosslinking agent, and (b) the partially neutralized copolymer of ethylene/acrylic acid at a temperature in the range of from about 110 to 130°C and then increasing the temperature to in excess of 135°C and mixing for a sufficient time to allow dynamic crosslinking.

13. A composition as claimed in any one of claims 1 to 12, which also contains a non-reactive thermoplastic resin.

14. A composition comprising (a) a carboxylated butadiene-acrylonitrile elastomer (b) an ethylene/acrylic acid copolymer, the acid groups of which are optionally partly neutralized, and (c) an epoxy compound having more than one epoxy moiety.

15. A composition as claimed in claim 14, the components of which are as specified in any one of claims 2 to 10.

16. A thermoplastic elastomer obtained by dynamic

crosslinking of the composition of claim 14 or claim 15.

17. A shaped article formed of the thermoplastic elastomer of claim 16.

18. A composition as claimed in claim 14 or an elastomer as claimed in claim 16, substantially as described in any one of the Examples herein with reference to any one of Samples 1 to 5, 7 to 10, 12 to 14, 16 to 18, 28 to 41 and 43 to 53.

19. A method of forming a thermoplastic elastomer carried out substantially as described in any one of the Examples herein with reference to any one of Samples 1 to 5, 7 to 10, 12 to 14, 16 to 18, 28 to 41 and 43 to 53.

20. Any new feature described herein, or any new combination of hereinbefore described features.